Abstract: Determination of adatom interaction energies by a Monte Carlo calculation: Oxygen on W(110)[a)]

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A great deal of experimental data on the order–disorder transition of the $p(2 \times 1)$ structure of oxygen on W(110) is available.[1–4] Previous attempts to determine the adatom–adatom interaction energies from different sets of these data have been made.[4,5] However, in both attempts a model for the interaction energies which was inconsistent with the symmetry of the surface was used.

The locations of the oxygen atoms in the $p(2 \times 1)$ structure on W(110) as determined by dynamical calculations of LEED I–V curves are shown in Fig. 1. The parameters ϵ_x denote the interaction energies between oxygen atoms which are separated by the arrows as shown. In the previous studies[4,5] the parameters ϵ_a, ϵ_b, and ϵ_{2b}, where ϵ_a and ϵ_{2b} are attractive interactions and ϵ_b is repulsive, were used. But since the (10) and $(0\bar{1})$ directions are equivalent, it is a violation of symmetry considerations to assign different values to ϵ_a and ϵ_b. Furthermore, if this were the true set of interaction energies only the domain shown in Fig. 1 would occur and not the domain in which the rows of adatoms are in the $(0\bar{1})$ direction. Both the $(\frac{1}{2}, 0)$ and $(0, \frac{1}{2})$ spots are observed experimentally indicating that both domains are present. Therefore, this model for the interaction energies cannot be correct.

The parameters used in this study, ϵ_1, ϵ_2, ϵ_3, and ϵ_4, where ϵ_1 and ϵ_4 are attractive and ϵ_2 and ϵ_3 are repulsive, conform to the symmetry of the surface and allow the formation of perpendicular domains. While ϵ_2 and ϵ_3 are undoubtedly different, they are set equal in this study since the data are insufficient to determine four parameters uniquely.

A Monte Carlo calculation using a 30×30 lattice with periodic boundary conditions was used to simulate equilibrium configurations of the adatoms as a function of temperature for various sets of interaction energies. The LEED beam intensities for these configurations were calculated within the kinematic approximation and the intensity versus temperature (I–T) curves thus generated were compared with the experimental data[4] to determine the best set of parameters. I–T curves were calculated for a large number of ratios of $\epsilon_1{:}\epsilon_2 = \epsilon_3{:}\epsilon_4$ at half coverage ($\theta = 0.5$). The parameters were then scaled to give the correct transition temperature ($T_c = 730$ K) at half coverage, and I–T curves were calculated for quarter coverage ($\theta = 0.25$). It was possible to eliminate many sets of parameters as they gave an incorrect transition temperature at quarter coverage.

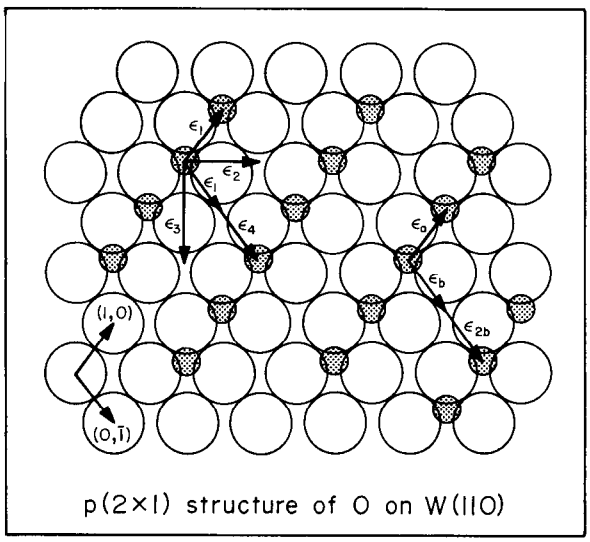

FIG. 1. Schematic of the $p(2 \times 1)$ overlayer of oxygen on W(110) as determined by LEED along with two possible models for the oxygen–oxygen interaction energies: (1) ϵ_1, ϵ_2, ϵ_3, and ϵ_4 which are used in this work; (2) ϵ_a, ϵ_b, and ϵ_{2b} which were used in Refs. 4 and 5.

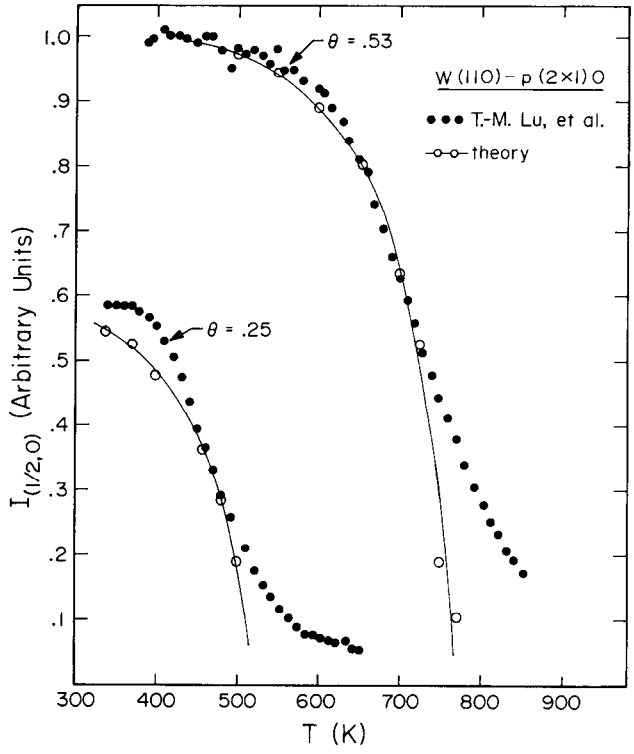

FIG. 2. Intensity of the $(\frac{1}{2}, 0)$ LEED spot for W(110)–$p(2 \times 1)$O as a function of temperature for two different coverages. The theoretical curve calculated using $\epsilon_1 = -2.1$ kcal/mol, $\epsilon_2 = \epsilon_3 = 1.7$ kcal/mol, and $\epsilon_4 = -0.7$ kcal/mol is compared with the experimental data from Ref. 4.

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The most satisfactory ratio of parameters is $\epsilon_1:\epsilon_2:\epsilon_4 = -1:{}^5/_6:-{}^1/_3$. The scaling factor which gives $T_c = 730$ K is 2.09 kcal/mol so that the final values are:

$\epsilon_1 = -2.1$ kcal/mol

$\epsilon_2 = \epsilon_3 = 1.7$ kcal/mol

$\epsilon_4 = -0.7$ kcal/mol.

Figure 2 shows a comparison of the I–T curves calculated using these parameters with the experimental data. The fit at $\theta = 0.53$ for temperatures below T_c is excellent. The poor fit above T_c is not considered important as the shape of the curve above the transition temperature is a strong function of lattice size.[7,8]

The values of the interaction energies determined in this study are of the order of magnitude expected.[9] They also show decrease in magnitude with distance, as opposed to earlier studies[4,5] in which ϵ_{2b}, the interaction energy between adatoms two lattice spacings apart was equal to ϵ_a, the interaction energy over one lattice spacing. Most important, these parameters are consistent with the symmetry requirements of the system.

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[1]J. C. Tracy and J. M. Blakely, Surf. Sci. **15,** 257 (1969).

[2]J. C. Buchholz and M. G. Lagally, Phys. Rev. Lett. **35,** 442 (1975).

[3]T. Engel, H. Niehus, and E. Bauer, Surf. Sci. **52,** 237 (1975).

[4]T.-M. Lu, G.-C. Wang, and M. G. Lagally, Phys. Rev. Lett. **39,** 411 (1977).

[5]G. Ertl and D. Schillinger, J. Chem. Phys. **66,** 2569 (1977).

[6]M. A. Van Hove and S. Y. Tong, Phys. Rev. Lett. **35,** 1092 (1975).

[7]D. P. Landau, Phys. Rev. B **13,** 2997 (1976).

[8]G. Doyen, G. Ertl, and M. Plancher, J. Chem. Phys. **62,** 2957 (1975).

[9]T. L. Einstein and J. R. Schrieffer, Phys. Rev. B **7,** 3629 (1973).